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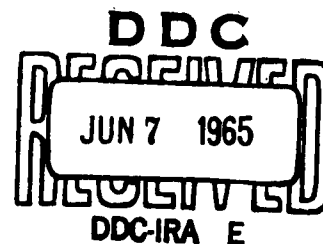
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TECHNICAL REPORT NO. 44



Nuclear Magnetic Resonance Spectroscopy.
Analysis and Temperature Dependence of the
Spectra of Cycloheptatriene and 7,7-Bistrifluoro-
methylcycloheptatriene.

By Joseph B. Lambert and John D. Roberts

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Nuclear Magnetic Resonance Spectroscopy. Analysis and Temperature
Dependence of the Spectra of Cycloheptatriene and 7,7-Bis(trifluoro-
methyl)cycloheptatriene¹

(1) Supported in part by the Office of Naval Research and the
National Science Foundation.

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and John D. Roberts

(2) National Science Foundation Predoctoral Fellow, 1962-1965.

(3) Stanford University, Stanford, California.

Contribution No. 3237 from the Gates and Crellin Laboratories of
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Received

Complete analyses of the room-temperature proton spectra of cycloheptatriene (I) and its 7,7-bis(trifluoromethyl) derivative (II) have been achieved. Whereas the methylene protons of I are nonequivalent below about -140° , the trifluoromethyl groups in II remain equivalent on the n. m. r. time scale down to -185° . An explanation for this behavior is sought in the differences in the magnitudes of the vicinal coupling constants (J_{23}) of I and II. There is no change in any of the coupling constants of I over the temperature range from -70 to $+115^{\circ}$. The n. m. r. evidence therefore gives no indication of the presence of norcaradiene in equilibrium with cycloheptatriene.

Introduction

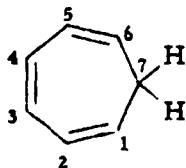
The isolation of tricyclic Diels-Alder adducts of cycloheptatriene (I)^{4, 5} and its unsubstituted carboxylic acid derivatives^{6, 7} and

(4) K. Alder and G. Jacobs, Ber., 86, 1528 (1953).

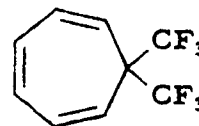
(5) N. W. Jordon and I. W. Elliott, J. Org. Chem., 27, 1445 (1962).

(6) K. Alder, H. Jungen, and K. Rust, Ann., 602, 94 (1957).

(7) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, J. Am. Chem. Soc., 78, 5448 (1956).



I

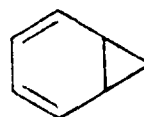
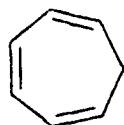


II

the oxidation of cycloheptatriene-7-carboxylic acid to trans-cyclopropane-1, 2, 3-carboxylic acid⁸ suggested that the cycloheptatriene

(8) W. Braren and E. Buchner, Ber., 34, 982 (1901).

system is in equilibrium with its valence tautomer, norcaradiene (III),



III

(1)

which is capable of independent reactions under particular conditions.⁹

(9) For a review of the many ramifications of this problem, see M. R. Willcott, Ph. D. Dissertation, Yale University, 1963.

Direct experimental observation of norcaradiene, however, has eluded the efforts of many workers. The challenge to construct bicyclo[4.1.0]heptadiene derivatives has resulted in the successful synthesis of several stable norcaradiene systems.¹⁰⁻¹⁷ Although the structure of

(10) W. von E. Doering and M. J. Goldstein, Tetrahedron, 5, 53 (1959).

(11) R. Darms, T. Threlfall, M. Pesaro, and A. Eschenmoser, Helv. chim. Acta, 46, 2893 (1963).

(12) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, Tetrahedron Letters, No. 11, 673 (1963).

(13) E. Vogel, D. Wendrick, and W. R. Roth, Angew. Chem., 76, 432 (1964).

(14) W. Tochtermann, U. Walter, and A. Mannschreck, Tetrahedron Letters, No. 40, 2981 (1964).

(15) E. Ciganek, J. Am. Chem. Soc., 87, 652 (1965).

(16) E. Müller, H. Kessler, and H. Suhr, Tetrahedron Letters, No. 8, 423 (1965).

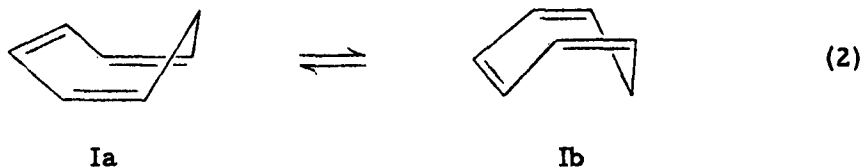
(17) G. E. Hall and J. P. Ward, ibid., No. 8, 437 (1965).

"tropilidene" has long been considered to be the monocyclic triene I,⁹ there has been some controversy over the question of planarity. The

equivalence of the methylene protons in the n. m. r. spectrum of cycloheptatriene at room temperature is consistent with a planar structure and with a rapidly oscillating pair of nonplanar conformers (Ia and Ib). Observation by Anet¹⁸ and later by Jensen and Smith¹⁹ of

(18) F. A. L. Anet, J. Am. Chem. Soc., 86, 458 (1964).

(19) F. R. Jensen and L. A. Smith, ibid., 86, 956 (1964).



separate resonances for the 7-protons below -140° provided unambiguous evidence in favor of the equilibrating pair of nonplanar conformers. The ring inversion process was characterized by an activation energy of about 6.0 kcal./mole. Traetteberg's electron diffraction study²⁰

(20) M. Traetteberg, ibid., 86, 4265 (1964).

furthermore showed that the plane determined by carbon atoms 1, 2, 5, 6 intersects the 1, 6, 7 plane with an acute angle of 36.5° and the 2, 3, 4, 5 plane with an angle of 40.5° .

The behavior of 7, 7-bistrifluoromethylcycloheptatriene (II)²¹

(21) D. M. Gale, W. J. Middleton, and C. G. Krespan, ibid., 87, 657 (1965). We are indebted to Dr. Gale for the generous sample of II which was used in the present investigation.

contrasts with that of the unsubstituted case, in that the trifluoromethyl groups remain equivalent down to -185° . The question of planarity again must be resolved. In this work we have analyzed the proton spectra of I and II and attempted an explanation of their conformational differences in terms of the magnitudes of the vicinal couplings (J_{23}). We also have examined the temperature dependence of the coupling constants of I for any vestige of evidence for norcaradiene.

Results

The proton spectrum of cycloheptatriene (Columbia Organic Chemicals Co.) was recorded on a Varian HA-60 spectrometer at -70 , $+26$, and $+115^{\circ}$ (carbon disulfide solution). The room-temperature spectrum of protons 2-5 is displayed in Figure 1. Transition frequencies were obtained from the average of four upfield and four downfield sweeps. Since the 1,6 protons are chemically shifted from the 2-5 protons by at least 45 c.p.s., the couplings between these sets of nuclei are considered to be first order. In fact, the AA'BB' spectrum of the 2-5 protons may be analyzed by disregarding these couplings (J_{12} , J_{13} , J_{14} , and J_{15}). The low-field multiplet is a quartet of triplets, the triplet structure arising from small couplings with the 1,6 protons. The high-field multiplet is a doublet of quartets, the doublet structure arising from a large coupling with the 1,6 protons. Thus, if the couplings with the 1,6 protons were disregarded, the resulting spectrum would consist primarily of two mirror-image quartets. This prediction was substantiated by a double-irradiation experiment (HR-100, field sweep), which collapsed the low-field multiplet to a quartet (Figure 2). The methylene protons have no effect on the

spectrum of the 3, 4 protons, but they have a small coupling with the 2, 5 protons which obscures the quartet nature of the multiplets. In the spectrum of 7, 7-dideuterocycloheptatriene,²² the splitting of the

(22) The authors are grateful to Professor W. von E. Doering, Yale University, New Haven, Connecticut, for furnishing a sample of this compound.

central peaks of each quartet was clearly defined.

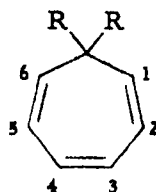
The four-spin system was analyzed according to the method of Swalen and Reilly.²³ It was immediately apparent that the splittings

(23) J. D. Swalen and C. A. Reilly, J. Chem. Phys., 37, 21 (1962).

which give rise to the quartets do not correspond directly to $J_{23}(J_{45})$ and $J_{24}(J_{35})$. If this were the case, $J_{34} = 0.0$, which is an unreasonable value for a cis-vinylic coupling. The complete analysis of the AA'BB' spectrum required the accurate assignment of low-intensity transitions in the wings (Figure 1). The resulting parameters are listed in Table I. The spectrum calculated from these parameters, with the couplings from the 1, 6 protons superimposed, is also given in Figure 1. The average deviation between the observed and calculated transitions is about 0.1 c. p. s. The errors in the coupling constants are also approximately ± 0.1 c. p. s.

The 100-Mc.p.s. proton spectrum of 7, 7-bistrifluoromethylcycloheptatriene (carbon tetrachloride solution) (Figure 3) consists of

Table I. Spectral Parameters for Cycloheptatriene and 7,7-Bis(tri-fluoromethyl)cycloheptatriene.



	I	II
δ_{23}^a	23.01 ^b	7.42 ^c
\underline{J}_{23}	5.26	6.86
\underline{J}_{24}	0.80	0.80
\underline{J}_{25}	0.0	0.10
\underline{J}_{34}	10.67	10.37
\underline{J}_{12}	8.58	—
\underline{J}_{13}	— ^d	—
\underline{J}_{14}	— ^d	—
\underline{J}_{15}	0.0	—
\underline{J}_{16}	—	—

^a All quantities are expressed in units of c. p. s.

^b 60 Mc. p. s.

^c 100 Mc. p. s.

^d $\underline{J}_{13} + \underline{J}_{14} = 1.56$ c. p. s.

a doublet from the 1, 6 protons and a multiplet lacking extensive fine structure from the 2-5 protons. This spectrum could not be analyzed. The closely coupled AA'BB' spectrum of the 2-5 protons was recorded on a Varian HA-100 spectrometer by irradiation (frequency sweep) of the 1, 6 protons²⁴ (Figure 4). The low-field resonances must arise

(24) We thank Leroy Johnson, Varian Associates, Palo Alto, California, for recording these spectra.

from the 2, 5 protons because of the presence of small couplings with the fluorine atoms. The analysis followed the method of Swalen and Reilly²³ after assignment of transitions by comparison with spectra published by Wiberg and Nist.²⁵ The resulting parameters are listed

(25) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, 1962.

in Table I, and the calculated spectrum is compared with the observed spectrum in Figure 4. The errors in the coupling constants are again about ± 0.1 c. p. s.

The A and B protons are so closely coupled that the 8 and 11 transitions²⁶ of the low-field protons overlap into the multiplet of the

(26) We use the convention described by J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, 1959, p. 144.

high-field protons. These "foreign" transitions, which happen to be degenerate, are designated a in Figure 4; the corresponding transitions belonging to the high-field protons, but located among the low-field transitions, are designated a'. Since the transitions a must be involved in couplings with the fluorine nuclei,²⁴ the observed peak a is of lower intensity than indicated by the calculated spectrum, which omitted such couplings. The presence of virtual couplings that broaden the a' transitions was demonstrated by calculation of the spectrum including a small coupling between the low-field protons and an imaginary X proton. Both the a and the a' transitions were perturbed, although the former to a greater extent.

The fluorine spectrum of II was examined at 56.4 Mc. p. s. on a Varian HR-60 spectrometer down to -185° (propene solution). At this temperature the trifluoromethyl groups were still equivalent. No substantial line broadening had occurred. Since fluorine-fluorine chemical-shift differences are generally an order of magnitude larger than the corresponding proton-proton chemical-shift differences, the barrier to ring inversion must be significantly lower in II than in I.

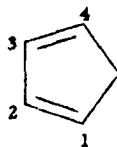
Discussion

Manatt and Elleman²⁷ have recently discussed the analyses

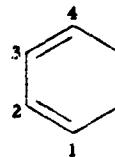
(27) S. L. Manatt and D. D. Elleman, to be published. We are grateful to Drs. Manatt and Elleman for permitting us to include portions of their results prior to publication.

of the spectra of the vinyl protons of cyclopentadiene (IV) and

cyclohexadiene (V) in terms of the relative importance of contributions



IV



V

to couplings through the σ -bond framework, through the π -electrons, and through space. Comparison of our results with theirs in Table II shows substantial agreement. We shall first discuss the long-range couplings found in the cycloheptatrienes, and then consider the question of planarity in terms of the three-bond couplings.

σ -Contributions to long-range couplings are typically less than 0.3 c. p. s.²⁷ According to Karplus,²⁸ the value of \underline{J} for couplings

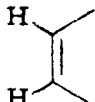
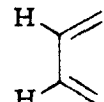
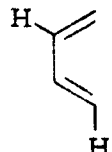
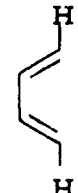

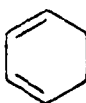

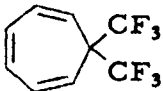
(28) M. Karplus, J. Chem. Phys., 33, 1842 (1960).

transmitted through the π -electrons will be positive if the coupled protons are separated by an odd number of bonds, and negative otherwise. For the four cases considered in Table II, all couplings appear to be positive. This argues for contributions to \underline{J}_{24} from sources other than through the π -system. Manatt and Elleman have suggested that there is a large positive contribution to the coupling from a mechanism similar to that operating in certain bicyclic systems.²⁹

(29) M. Barfield, ibid., 41, 3825 (1964).

The lower values for \underline{J}_{25} in both I and II may then be ascribed to an

Table II. Comparison of Coupling Constants in Cyclopentadiene, Cyclohexadiene, Cycloheptatriene, and Bistrifluoromethylcycloheptatriene.

				
	5.06 ^a	1.94	1.09	1.94
	9.42	5.14	1.06	0.91
	10.67 ^b	5.26	0.80 ^c	0.0 ^d
	10.37 ^b	6.86	0.80 ^c	0.10 ^d

^a All quantities are expressed in units of c. p. s.

^b J_{34} .

^c J_{24} .

^d J_{25} .

unfavorable relative orientation of the C-H bonds. However, there is a noticeable decrease in the five-bond couplings with increasing ring size. Thus, J_{14} is 1.94 c.p.s. in cyclopentadiene and 0.91 c.p.s. in cyclohexadiene, but J_{25} is close to zero in the cycloheptatrienes. This may be interpreted as resulting either from changes in the nature of the π -bonds with ring size, or from the decrease of a through-space coupling as the intra-carbon distance increases. Only the sum of the long-range couplings (J_{13} and J_{14}) which give rise in I to the triplet structure of the low-field resonances (Figure 1) is available, since the criterion for a deceptively simple spectrum appears to apply to this case.³⁰

(30) R. J. Abraham and H. J. Bernstein, Can. J. Chem., 39, 216 (1961).

Various workers³¹⁻³⁴ have demonstrated that the cis-vinylc

(31) O. L. Chapman, J. Am. Chem. Soc., 85, 2014 (1963).

(32) G. V. Smith and H. Kriloff, ibid., 85, 2016 (1963).

(33) P. Laszlo and P. von R. Schleyer, ibid., 85, 2017 (1963).

(34) S. Borčić and J. D. Roberts, ibid., 87, 1056 (1965).

couplings decrease rapidly with ring size. The effect of ring contraction probably accounts for the anomalous values of J_{12} and J_{23} in cyclopentadiene (Table II). The cis-vinylc coupling is rather constant for ring systems with more than six members.³² Provided substituent changes are not extensive, the magnitudes of analogous couplings

in a series of compounds with the same cyclic framework should remain constant. Thus, J_{14} is 10.67 c. p. s. in I and 10.37 c. p. s. in II. Conformational changes may be influential in the magnitudes of vicinal couplings between protons attached to sp^2 centers connected by a single bond (J_{23}). Since the relationship of Karplus appears to hold for vicinal couplings in medium rings,³² the magnitude of J_{23} should increase as the dihedral angle, which is necessarily acute, decreases. The increase of J_{23} from 5.26 c. p. s. in I to 6.86 c. p. s. in II speaks for a more nearly planar ring in the latter case. The decrease in puckering associated with 7,7-substitution in II must lower the barrier to ring inversion enough to prevent "freezing out" of a nonplanar conformer even at -185° .

The complete analysis of cycloheptatriene was also carried out at -70° and $+115^\circ$. No changes were observed in the coupling constants. An equilibrium between I and III would have been detected by variations of the couplings. Thus, large changes have been observed in the vicinal coupling constants in unsymmetrical cyclobutanes, which possess nonequivalent conformations.³⁵ The equilibrium observed by Anet¹⁸

(35) J. B. Lambert and J. D. Roberts, J. Am. Chem. Soc., in press.

and by Jensen and Smith¹⁹ must therefore be between species of equal energy, as expected from the model depicted in equation 2. Equilibria analogous to that between cycloheptatriene and norcaradiene have been observed by Vogel³⁶ and by Ciganek.³⁷ The present data exclude any

(36) E. Vogel, W. A. Böll, and H. Günther, Tetrahedron Letters, No. 10, 609 (1965).

(37) E. Ciganek, J. Am. Chem. Soc., 87, 1149 (1965).

but minute contributions from the equilibrium $I \rightleftharpoons III$ even at -70° .

Figure 1. The observed (above) and calculated 60.0-Mc.p.s. spectra of the 2, 3, 4, 5 protons of cycloheptatriene at 26°. The field increases from left to right in all spectra.

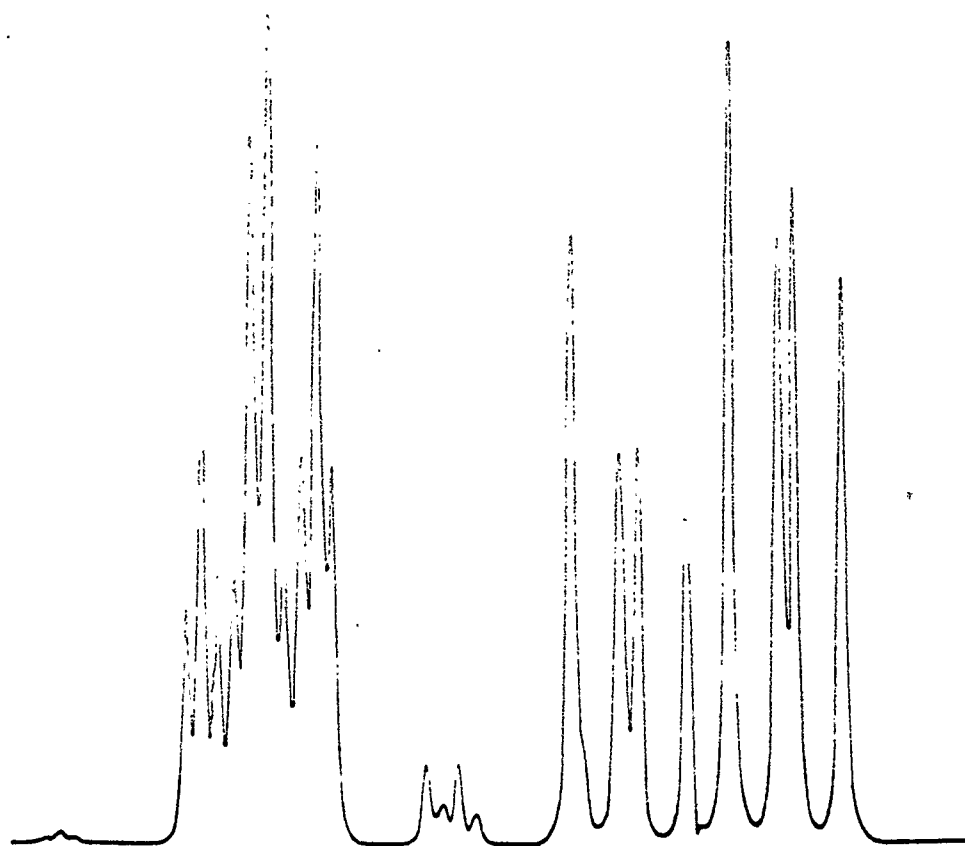
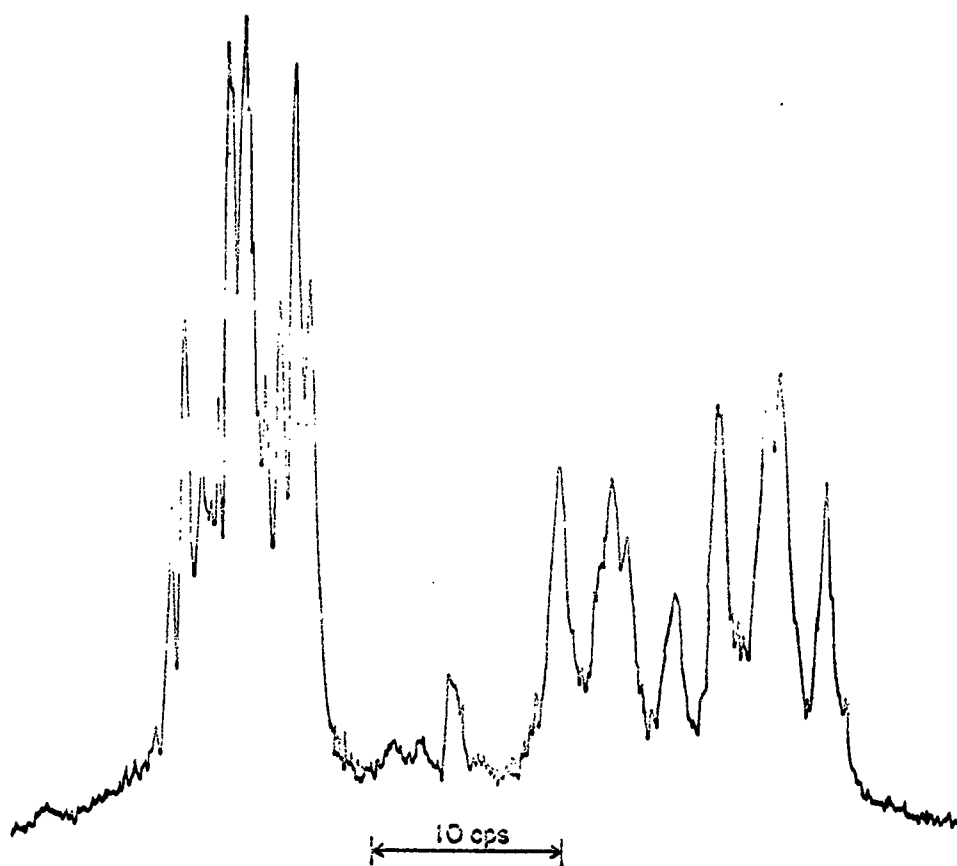


Figure 2. The 100-Mc.p.s. spectrum of the 3,4 protons of 7,7-di-deuterocycloheptatriene, with double irradiation of the 1,6 protons.

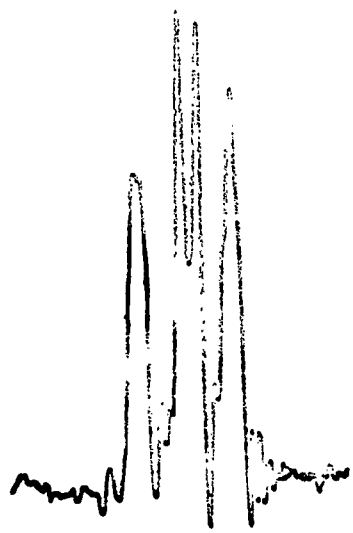


Figure 3. The 100.0-Mc. p. s. proton spectrum of 7,7-bistrifluoromethylcycloheptatriene.

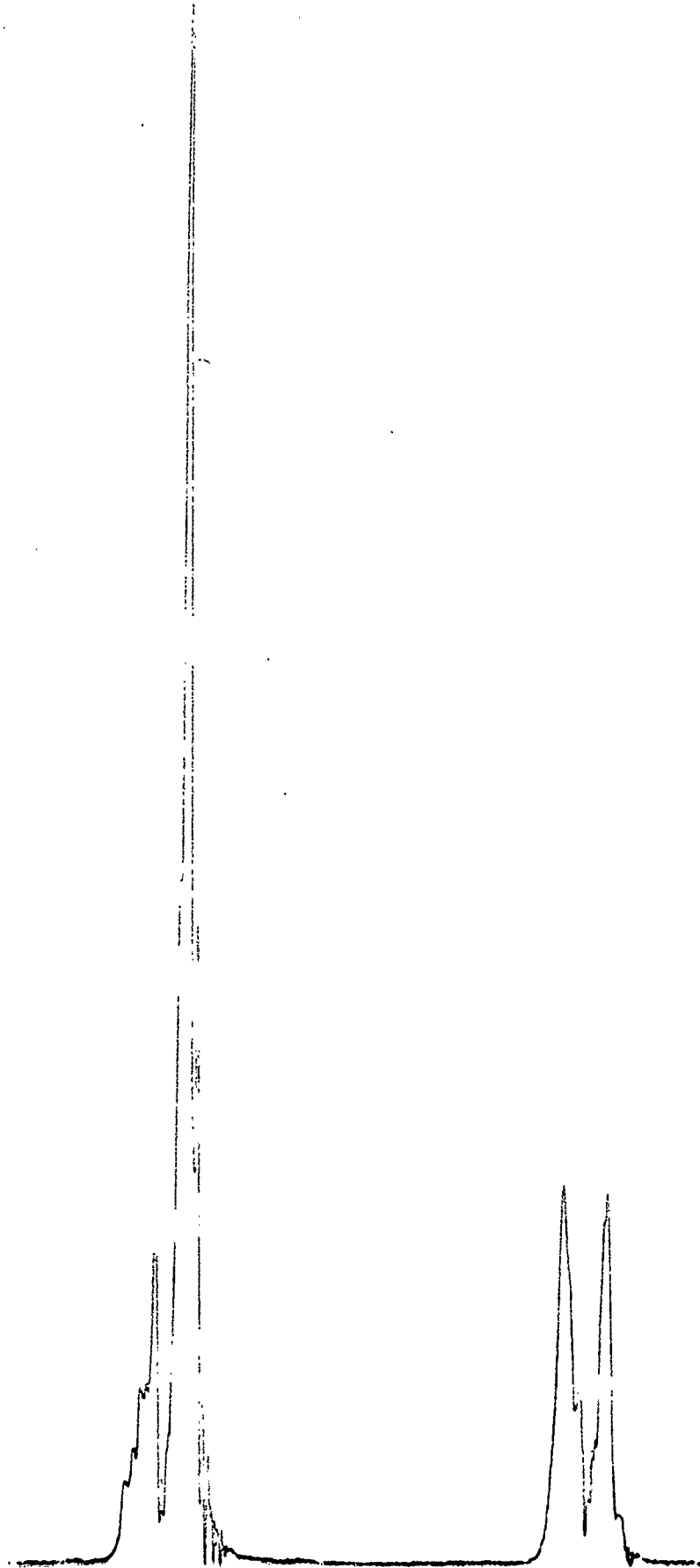
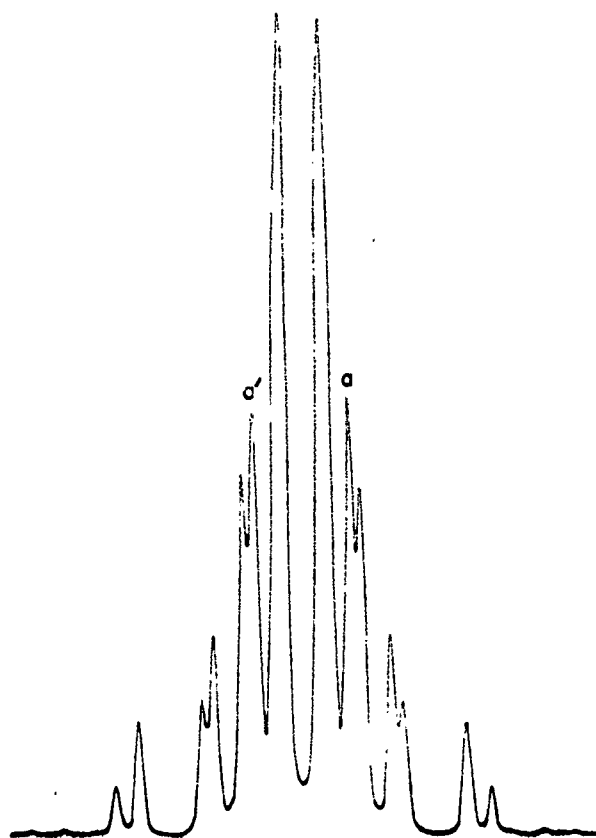
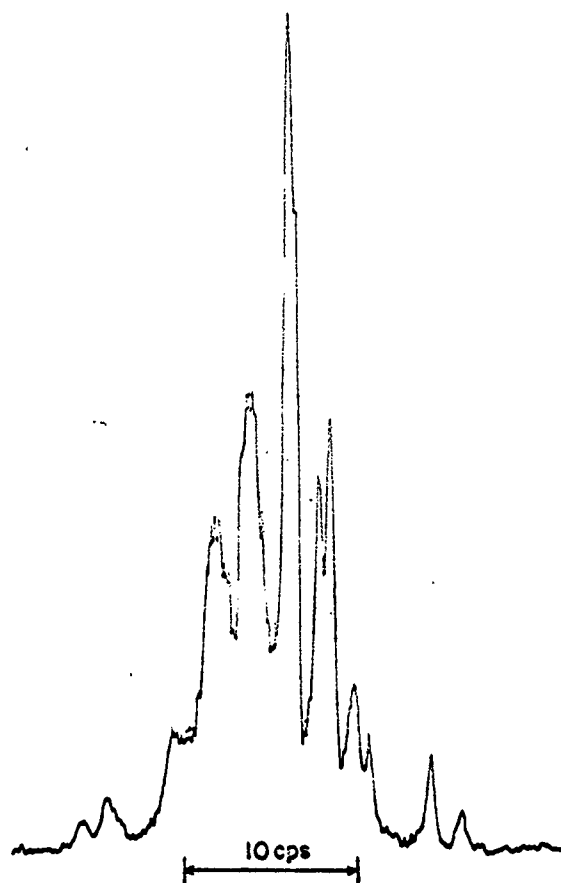


Figure 4. The observed (above) and calculated 100.0-Mc. p. s. spectra of the 2, 3, 4, 5 protons of 7, 7-bistrifluoromethylcycloheptatriene, with double irradiation of the 1, 6 protons.



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13. ABSTRACT			
<p>Complete analyses of the room-temperature proton spectra of cycloheptatriene (I) and its 7,7-bistrifluoromethyl derivative (II) have been achieved. Whereas the methylene protons of I are nonequivalent below about -140°, the trifluoromethyl groups in II remain equivalent on the n. m. r. time scale down to -185°. An explanation for this behavior is sought in the differences in the magnitudes of the vicinal coupling constants (J_{23}) of I and II. There is no change in any of the coupling constants of I over the temperature range from -70° to $+115^\circ$. The n. m. r. evidence therefore gives no indication of the presence of norcaradiene in equilibrium with cycloheptatriene.</p>			

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